1317731

PATENT SPECIFICATION

(11) 1317731

DRAWINGS ATTACHED

(21) Application No. 18161/70 (22) Filed 16 April 1970

(31) Convention Application No. 816764 (32) Filed 16 April 1969 in

(33) United States of America (US)

(44) Complete Specification published 23 May 1973

(51) International Classification H05B 33/12

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C4S 311 33Y 43Y 68X 68Y 708 709 70Y 711 714 715 717 731 733 735 739 753 757 75Y 764 767 768 76Y 770 771 782 78Y

(19) THE PATENT OFFICE LONDON

PATENTS ACT 1949

SPECIFICATION NO 1317731

Reference has been directed, in pursuance of Section 9, subsection (1) of the Patents Act 1949, to Specification No 1263185

THE PATENT OFFICE
1 February 1974

R 72294/4

... to be performed, to be particularly described in and by the following statement:—

The invention relates to electroluminescent apparatus. Contemplated use is in display devices on communication and computer equipment.

A variety of low power level, electroluminescent apparatus has been described. One such electroluminescent apparatus is described and claimed in British Patent Specification No. 18162/70 (Serial No. 1,317,732). This patent claims an electroluminescent device for producing radiation in the visible spectrum including a semiconductor PN junction diode capable of producing infrared radiation when biased, said diode being provided with a phosphor on a surface thereof for converting said infrared radiation to radiation in the visible spectrum, the said phosphor consisting of an oxyhalide and/or a fluorohalide host material, the halide in the fluorohalide being other than fluoride, and containing at least 5 cation percent of Yb^{3+} based on the total cation content of the phosphor, in which either the phosphor contains at least two anion sites per unit cell which are differently populated in at least one percent of the unit cells of said phosphor, or there is at least one anion vacancy per unit cell in at least one percent of the unit cells of the said phosphor, and wherein the phosphor further contains at least one of the following cations in the specified concentration ranges selected from the group which consists of from 1/16 cation % Er^{3+} to 20 cation % Er^{3+}, from 1/50

... of devices depends on the use of an up-converting phosphor coating on a gallium arsenide junction diode. This was recently described in an article by S. V. Galginaitis, et al, International conference on GaAs, Dallas, 17th October, 1968, "Spontaneous Emission Paper No. 2". The device depends on a phosphor coating which depends upon the presence of ytterbium acting as a sensitizer and erbium acting as an activator. Conversion from the infrared output of the GaAs junction to a green wavelength is brought about by a sequential (or second photon) process.

GaP devices containing both types of doping may simultaneously emit at green and red wavelengths. Since the red emission eventually saturates with increasing power while the green does not, the possibility of varying apparent colour output by varying input power is implicit. Since, however, red emission is also significantly more efficient, the likelihood of producing a dominant green output is small. Little if any attention has been directed to such an adjustable colour GaP device in the literature.

Coated GaAs devices described in the literature have invariably operated with output in the green.

In accordance with the invention there is provided an electroluminescent apparatus for producing radiation in the visible spectrum including an electroluminescent device comprising a semiconductor PN junction diode capable of producing infrared radiation within the absorption spectrum for Yb^{3+} when biased, said diode being provided with a phos-

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(72) Inventors SHOBHA SINGH and LEGRAND GERARD VAN UITERT

(54) ELECTROLUMINESCENT APPARATUS

(71) We, WESTERN ELECTRIC COMPANY, INCORPORATED, of 195 Broadway, New York City, New York State, United States of America, a Corporation organised and existing under the laws of the State of New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to electroluminescent apparatus. Contemplated use is in display devices on communication and computer equipment.

A variety of low power level, electroluminescent apparatus has been described. One such electroluminescent apparatus is described and claimed in British Patent Specification No. 18162/70 (Serial No. 1,317,732). This patent claims an electroluminescent device for producing radiation in the visible spectrum including a semiconductor PN junction diode capable of producing infrared radiation when biased, said diode being provided with a phosphor on a surface thereof for converting said infrared radiation to radiation in the visible spectrum, the said phosphor consisting of an oxyhalide and/or a fluorohalide host material, the halide in the fluorohalide being other than fluoride, and containing at least 5 cation percent of Yb^{3+} based on the total cation content of the phosphor, in which either the phosphor contains at least two anion sites per unit cell which are differently populated in at least one percent of the unit cells of said phosphor, or there is at least one anion vacancy per unit cell in at least one percent of the unit cells of the said phosphor, and wherein the phosphor further contains at least one of the following cations in the specified concentration ranges selected from the group which consists of from 1/16 cation % Er^{3+} to 20 cation % Er^{3+}, from 1/50 cation % Ho^{3+} to 5 cation % Ho^{3+}, and 1/16 cation % Tm^{3+} to 5 cation % Tm^{3+}.

The best publicized PN junction electroluminescent devices utilize gallium phosphide. Depending on which of the popular dopants, oxygen or nitrogen is used, these diodes may emit at red or green wavelengths.

A recently announced class of devices depends on the use of an up-converting phosphor coating on a gallium arsenide junction diode. This was recently described in an article by S. V. Galginaitis, et al, International conference on GaAs, Dallas, 17th October, 1968, "Spontaneous Emission Paper No. 2". The device depends on a phosphor coating which depends upon the presence of ytterbium acting as a sensitizer and erbium acting as an activator. Conversion from the infrared output of the GaAs junction to a green wavelength is brought about by a sequential (or second photon) process.

GaP devices containing both types of doping may simultaneously emit at green and red wavelengths. Since the red emission eventually saturates with increasing power while the green does not, the possibility of varying apparent colour output by varying input power is implicit. Since, however, red emission is also significantly more efficient, the likelihood of producing a dominant green output is small. Little if any attention has been directed to such an adjustable colour GaP device in the literature.

Coated GaAs devices described in the literature have invariably operated with output in the green.

In accordance with the invention there is provided an electroluminescent apparatus for producing radiation in the visible spectrum including an electroluminescent device comprising a semiconductor PN junction diode capable of producing infrared radiation within the absorption spectrum for Yb^{3+} when biased, said diode being provided with a phos-

phor on a surface thereof for converting the infrared radiation to radiation in the visible spectrum said phosphor containing the cation pair Yb^{3+}—Er^{3+}, wherein the said phosphor has either at least two anion sites per unit cell which are differently populated in at least one percent of the unit calls of the said phosphor, or at least one anion vacancy per unit cell in at least one percent of the unit cells of the phosphor and wherein the phosphor consists of a fluorohalide, the halide in the fluorohalide being other than fluoride, or an oxyhalide or a mixture thereof, the phosphor containing either a cation percent of from 1/16 cation % Er^{3+} to 20 cation % Er^{3+} and from 5 cation % Yb^{3+} to 50 cation % Yb^{3+}, or from 1/16 cation % Er^{3+} to 20 cation % Er^{3+} and 1/50 cation % Ho^{3+} to 5 cation % Ho^{3+} together with at least 5 cation % Yb^{3+} and in which the said phosphor is capable of converting said infrared radiation to visible emission by at least a two excitation process each producing a different emission wavelength and each of which process involves a multiphoton process which is at least a two stage excitation, and in which the electroluminescent device is in combination with a circuit for varying the power level of said infrared radiation so as to alter the relative amounts of visible radiation produced by the said two processes.

Throughout the specification it is intended that the Yb, Er and Ho concentration ranges as above, apply independently to each of the fluorohalide and oxyhalide components when in a mixture.

Compounds are exemplified by various oxyhalide stoichiometries in which the halide to oxygen ratio equals or exceeds unity and fluorohalides. As in known coated GaAs diodes, up conversion results from inclusion of trivalent ytterbium which serves as a sensitizer. This sensitizer ion is invariably paired with an activator which may be trivalent erbium or trivalent erbium and trivalent holmium.

For a better understanding of the invention, reference is made to the accompanying drawing in which:

FIG. 1 is a front elevational view of an infrared emitting diode having a phosphor converting coating in accordance with an embodiment of the invention; and

FIG. 2 is an energy level diagram in ordinate units of wave numbers for the ions Yb^{3+}, Er^{3+} and Ho^{3+} within the crystallographic environment provided by a composition herein.

Referring to FIG. 1, gallium arsenide diode 1 containing PN junction 2, defined by P and N regions 3 and 4, respectively, is forward-biased by planar anode 5 and ring cathode 6 connected to a power supply not shown. Infrared radiation is produced by junction 2 under forward-biased conditions, and some of this radiation, represented by arrows 7, passes into and through layer 8 of a phosphorescent material in accordance with the embodiment. Under these conditions, some part of radiation 7 is absorbed within layer 8, and a major portion of that absorbed participates in a two-photon or higher order photon process to produce radiation at visible wavelengths. The portion of this reradiation which escapes is represented by arrows 9.

Potentiometer 10, in series with diode 1, serves the function of permitting adjustment of input power to the diode thereby varying the infrared emission and, in consequence altering the apparent colour output of emission 9 in accordance with the embodiment. This element is intended to be illustrative of variable power input means which may be operated to adjust or alter apparent output frequency on occasion, in a continuous fashion or in any other desired manner.

The main advantage of the defined phosphors is best described in terms of the energy level diagram of FIG. 2. While this energy level diagram is a valuable aid in the description of the embodiment, two reservations must be made. The specific level values, while reasonably illustrative of those for the various included compositions of the noted type, are most closely representative of the oxychloride systems either of the YOCl or Y_3OCl_7 stoichiometries. Also, while the detailed energy level description was determined on the basis of carefully conducted absorption and emission studies, some of the information contained in the figure is not certain. In particular, the excitation routes for the 3 and 4 photon processes are not certain although it is clear that some of the observed emission represents a multiple photon process in excess of doubling. The diagram is sufficient for its purpose; that it, it does describe the common advantage of the included host materials and, more generally, of the included phosphors in the terminology which is in use by quantum physicists.

FIG. 2 contains information on Yb^{3+}, Er^{3+} and Ho^{3+}. The ordinate units are in wavelengths per centimetre (cm^{-1}). These units may be converted to wavelengths in angstrom units (Å) or microns (μ) in accordance with the relationship:

$$\text{Wavelength} = \frac{10^8}{\text{Wave numbers}}\,\text{Å} = \frac{10^4}{\text{Wave numbers}}\,\mu.$$

The left-hand portion of the diagram is concerned with the relevant manifolds of Yb^{3+} in a host of the embodiment. Absorption in Yb^{3+} results in an energy increase from the ground manifold $Yb^2F_{7/2}$ to the $Yb^2F_{5/2}$ manifold. This absorption defines a band which includes levels at 10,200cm^{-1}, 10,500cm^{-1}, and 10,700cm^{-1}. The positions of these levels are affected by the crystal field splitting within the structures having at least one each of two different anions or at least one anion vacancy per unit cell or formula unit. In the oxychlorides, for example, they include a broad absorption which peaks at about 0.935μ (10,700cm^{-1}), there is an efficient transfer of energy from a silicon-doped GaAs diode (with its emission peak at about 0.93μ). This contrasts with the comparatively small splitting and weaker absorption at 0.93μ in lanthanum fluoride and other less anisotropic previously known hosts in which absorption peaking is at about 0.98μ for Yb^{3+}.

The remainder of FIG. 2 is discussed in conjunction with the postulated excitation mechanism All anergy level values and all relaxations indicated on the figure have been experimentally verified.

Following absorption by Yb^{3+}, of emission from the GaAs diode, a quantum is yielded to the emitting ion Er^{3+} (or as also discussed in conjunction with the figure, to Ho^{3+}). The first transition is denoted 11. Excitation of Er^{3+} to the $^4I_{11/2}$ is almost exactly matched in energy (denoted by m) to the relaxation transition of Yb^{3+}. However, a similar transfer, resulting in excitation of Ho^{3+} to Ho^5I_6 requires a simultaneous release of one or more phonons (+P). The manifold $Er^4I_{11/2}$ has a substantial lifetime, and transfer of a second quantum from Yb^{3+} promotes transition 12 to the $Er^4F_{7/2}$ manifold. Transfer of a second quantum to Ho^{3+} results in excitation to Ho^5S_2 with simultaneous generation of a phonon. Internal relaxation is represented on this figure by the wavy arrow (↘). In erbium, the second photon level ($Er^4F_{7/2}$) has a lifetime which is very short due to the presence of close, lower lying levels which results in rapid degradation to the $Er^4S_{3/2}$ state through the generation of phonons.

The first significant emission of Er^{3+} is from the $Er^4S_{3/2}$ state (18,200cm^{-1} or 0.55μ in the green). This emission is denoted in the figure by the broad (double line) arrow A. The reverse of the second photon excitation, the nonradiative transfer of a quantum from $Er^4F_{7/2}$ back to Yb^{3+} must compete with the rapid phonon relaxation to $Er^4S_{3/2}$ and is not limiting. The phonon relaxation to $Er^2F_{9/2}$ also competes with emission A and contributes to emission from that level. The extent to which this further relaxation is significant is composition dependent.

In accordance with this embodiment, it has been shown that the structures having mixed anions or anion vacancies with large resulting anisotropic environments about the cations are characterized by large crystal field splitting and improved absorption of GaAs: Si emission by Yb^{3+}. Large crystal field anisotropics also result in increased opportunity for internal relaxation mechanisms involving phonon generation which thus far have not been found to be pronounced in comparable but more isotropic media. For Er^{3+}, this enhances emission B at red wavelengths. Erbium emission B is, in part, brought about by transfer of a third quantum from Yb^{3+} to Er^{3+} which excites the ion from $Er^4S_{3/2}$ to $Er^2G_{7/2}$ with simultaneous generation of a phonon (transition 13). This is followed by internal relaxation to $Er^4G_{11/2}$ which, in turn, permits relaxation to $Er^2F_{9/2}$ by transfer of a quantum back to Yb^{3+} with the simultaneous generation of a phonon (transition 13'). The $Er^2F_{9/2}$ level is thereby populated by at least two distinct mechanisms and indeed experimental confirmation arises from the finding that emission B is dependent on a power of the input intensity which is intermediate in character to that characteristic of a three-phonon process and that characteristic of a two-phonon process for a Y_3OCl_7 host. Emission B, in the red, is at about 15,250cm^{-1} or 0.66μ.

While emissions in the green and red are predominant, there are many other emission wavelengths of which the next strongest designated C is in the blue (24,400cm^{-1} or 0.41μ). This third emission designated C originates from the $Er^2H_{9/2}$ level which is, in turn, populated by two mechanisms. In the first of these, energy is received by a phonon process from $Er^4G_{7/2}$. The other mechanism is a four-photon process in accordance with which a fourth quanta is transferred by Yb^{3+} to Er^{3+} exciting $Er^4G_{9/2}$ from $Er^4G_{11/2}$ (transition 14). This step is followed by internal relaxation to $Er^2D_{5/2}$ from which level energy can be transferred back to Yb relaxing Er to $Er^2H_{9/2}$ (transition 14').

Significant emission from holmium occurs only by a two-photon process. Emission is predominantly from Ho^5S_2 in the green (18,350cm^{-1} or 0.54μ). The responsible mechanisms are clear from FIG. 2 and the foregoing discussion.

Since the phosphors of the embodiments are in powder or polycrystalline form, growth presents no particular problem. Oxychlorides, for example, may be prepared by dissolving the oxides (rare earth and yttrium oxides) in hydrochloric acid, evaporating to form the hydrated chlorides, dehydrating, usually near 100°C under vacuum, and treating with Cl_2 gas at an elevated temperature (about 900°C). The resulting product can be the one or more oxychlorides, a trichloride or mixtures of these depending on the dehydrating conditions, vacuum integrity and cooling conditions. The

trichloride melts at the elevated temperature and may act as a flux to crystallize the oxychlorides. The YOCl host structure is favoured by high Y contents, intermediate dehydration rates and slow cooling rates, while more complex chlorides are favoured by high rare earth content, slow dehydration and fast cooling. The trichloride is subsequently removed by washing with water. Dehydration should be sufficiently slow (usually 5 minutes or more) to avoid excessive loss of chlorine.

Oxybromides and oxyiodides may be prepared by similar means using hydrobromic acid and gaseous HBr or hydroiodic acid and gaseous HI in place of hydrochloric acid and Cl_2 in the process.

Lead or alkaline earth fluorochlorides and fluorobromides may be prepared simply by melting the appropriate halides together. The products can, in turn, be melted together with the oxyhalide phosphors to adjust their properties.

The compositional requirements of the embodiments have been briefly set forth. Adjustability or tunability depend upon the crystal field conditions which have been observed in a number of compounds wherein the rare earth ion is in an anisotropic environment. This anisotropy results by use of a host composition which includes at least one compound having a crystalline structure such that there are at least two available anion sites per unit cell which are populated differently in at least 1% of the unit cells and preferably in at least 5% of the unit cells or a compound in which one such site is occupied while the other is not. Examples of such compounds are: rare earth and yttrium oxychlorides, oxybromides, oxyiodides, and mixtures of oxyhalides with fluorohalides.

The oxychlorides, oxybromides and oxyiodides are preferred; and, of these, the oxychlorides are the most preferred class. These include at least two different stoichiometries which may be designated in accordance with their chlorine to oxygen ion ratios. The simplest stoichiometry exemplified by YOCl has the tetragonal

$$D\frac{7}{4h}-P4/nmm$$

structure. A different stoichiometry has a hexagonal structure. An exemplary material has a composition with the analysed metal ratios: Y=56%, Yb=43% and Er=1%, has lattice constants $a_0=5.607$, $c_0=0.260$ and has prominant d-spacings of 9.20, 2.33, 3.09, 4.62 and 2.83. Analysis indicates the structure M_3OCl_7 where M is one or more of the cations of the rare earths, with ytterbium and erbium additives.

For the purposes of discussion of the embodiment, oxychlorides are discussed in terms of a first class in which the chlorine to oxygen cation content is approximately equal to unity and a second class in which the chlorine to oxygen cation ratio is greater than unity. In accordance with the said second class, a ratio of at least 1.5 is considered to suffice.

Every composition in accordance with these embodiments contains the cation pair Yb^{3+}—Er^{3+} although, as noted, this may be modified by addition of Ho^{3+}. Yb^{3+} is the required sensitizer and it is to this ion that initial energy transfer is first made from the infrared diode. A minimum Yb^{3+} content is 5% since appreciably less Yb^{3+} is insufficient to result in reasonable conversion efficiency regardless of Er^{3+} content. A preferred minimum of about 10% on the same basis is based on an observed output intensity comparable to that of well engineered gallium phosphide diodes. These minima applied universally to the total phosphor compositions of the embodiments.

The maximum recommended Yb^{3+} content is somewhat dependent upon the other nature of the phosphor composition. To some extent, this fact is evident from the detailed description of FIG. 2. Regardless of the nature of the composition, a Yb^{3+} content of 50% is permitted in the absence of Ho additions. A content approaching 100% (allowing for activator) is permitted when Ho is present. The 50% content is not sufficiently high to mask an otherwise obtainable green emission by employing an adequate Er^{3+} content and the presence of Ho^{3+} assures green emission at low power levels for any Yb^{3+} content. Specific maxima are discussed in terms of two systems.

Oxyhalides containing X:O ratios of at least 1.5, X being the halogen.

For compositions activated by Er^{3+} alone the maximum Yb^{3+} content is 50% of the cations since beyond this level multiphoton processes in excess of two photons become sufficiently efficient under many conditions to limit green emission. A preferred maximum lies at 40% since essentially pure green remains attainable from Er^{3+} for the usual range of content of this ion at some GaAs emission output level. However, for compounds co-activated by at least 1/50 cation % Ho^{3+} the upper Yb^{3+} limit approaches 100% (allowing only for activator).

Those including oxyhalide in which the X:O anion ratio is approximately 1:1, X being the halogen.

These compounds emit red when sensitized by Yb^{3+} and activated by Er^{3+}. The upper limit of Yb^{3+} approaches 100% (allowing for activator) when Er^{3+} and Ho^{3+} are present.

Er^{3+} content is selected to maximize brightness for this is the principal activator present, although other considerations dictate limits.

The erbium content is from 1/16% to 20%. Below this minimum, brightness is not appreciable. Above the maximum, radiationless processes substantially quench output. A preferred range is from about 1/4% to about 2%. The minimum is dictated by the subjective criterion that only at this level does a coated diode with sufficient brightness for observation in a normally lighted room result. The upper limit results from the observation that further increase does not substantially increase output.

Holmium, recommended as an adjunct to erbium in conjunction with ytterbium, may be included in an amount from about 1/50% to 5% to enhance the green output of erbium.

In addition to Yb+Er+Ho, "diluent" cations may be included. Such cations desirably have no absorption levels below any of the levels relevant to the described multiphoton processes. A cation which has been found suitable is yttrium. Others include Pb^{2+}, Gd^{3+} and Lu^{3+} have been set forth above.

Other requirements are common to phosphor materials in general. Various impurities which may produce unwanted absorption or which may otherwise "poison" the systems are to be avoided. As a general premise, maintaining the compositions at a purity level resulting from use of starting ingredients which are three nines pure (99.9%) is adequate. Further improvement, however, results from further increase in purity at least of five nines level. For long term use many of the included compositions are desirably protected from certain environmental constituents. Glass, plastic, and other common incapsulants are suitably used for such purpose.

The following examples are directed to a combination of a silicon-doped GaAs diode with a phosphor or a combination of phosphors that appear to emit visible light that can be varied in colour by changing the intensity of emission from the diode. The diode employed had a 25 mil junction and a 72 mil dome. For 1.5 volts applied as a forward bias with a resulting 2 amps passing through the diode the output of the diode was 0.2 watts at 0.93μ. In each case the phosphor or combination of phosphors was applied directly to the diode dome as a 2 mil thick film using collodion as a binder. A constant voltage supply set for one volt was used to supply current to the diode. The principal emissions affecting the eye are red (at 0.66μ) and green (in the 0.54—0.55μ region). As the former is the product of a three-photon process that drains the levels responsible for green emission in Er and the latter is a two-photon process for both Er and Ho, the relative intensity of emission in the red increases rapidly with increasing diode emission (or increasing current through the diode). To the eye, the apparent hue of the overall emission can thereby be varied from blue green to red including the intermediate shades.

Example 1

Using a phosphor $(Yb_{0.29}Er_{0.01}Y_{0.70})_3OCl_7$ the apparent emission was green below 0.1 amp, red above 0.5 amps and changed in hue through the yellowish white in between.

Example 2

Using the phosphor

$$(Yb_{0.29}Er_{0.01}Ho_{0.0005}Y_{0.6995})_3OCl_7$$

the apparent emission was green below 0.2 amps, red above 0.6 amps and changed in hue in between.

The compositions listed below constitute additional examples of materials colourable under conditions similar to those of examples 1 and 2.

$(Y_{0.7}Yb_{0.29}Er_{0.01})_3OCl_7$

$(Y_{0.7}Yb_{0.29}Er_{0.01})_3OCl_6Br$

$(Y_{0.7}Yb_{0.29}Er_{0.01})_3OCl_6I$

$(Y_{0.7}Yb_{0.29}Er_{0.01})_3OCl_6F$

$(Gd_{0.7}Yb_{0.29}Er_{0.01})_3OCl_7$

$(La_{0.7}Yb_{0.29}Er_{0.01})_3OCl_7$

$(Lu_{0.7}Yb_{0.29}Er_{0.01})_3OCl_7$

$(Y_{0.7}Yb_{0.2895}Er_{0.01}Ho_{0.0005})_3OCl_7$

$Yb_{0.975}Er_{.02}Ho_{.005}OCl$

$Yb_{0.975}Er_{.02}Ho_{.005}OBr$

$Yb_{0.975}Er_{.02}Ho_{.005}OI$

$Y_{.5}Yb_{.475}Er_{.02}Ho_{.005}OCl$

$Y_{.5}Yb_{.475}Er_{.02}Ho_{.005}OBr$

$Y_{.5}Yb_{.475}Er_{.02}Ho_{.005}OI$

$1/2\ Yb_{0.979}Er_{.02}Ho_{.001}OCl \,.\, 1/2NaY_{.7}Yb_{.29}Er_{.01}F_2Cl_2$

$1/2\ Yb_{0.979}Er_{.02}Ho_{.001}OCl \,.\, 1/2\ NaLa_{.7}Yb_{.29}Er_{.01}F_2Cl_2$

$1/2\ Yb_{0.979}Er_{.02}Ho_{.001}OCl \,.\, 1/2\ NaGd_{.7}Yb_{.29}Er_{.01}F_2Cl_2$

The above concept is of immediate value for use in coated GaAs diodes along with such means as to provide adhesion, minimize scattering and protect from the environment and such embodiment is preferred. Nevertheless, this is believed to be the first phosphor system from which a variety of apparent visible colours may be expediently produced by up conversion from infrared energy.

Since the above concept is dependent upon the apparent change in colour output of the phosphor, apparatus in accordance with the invention necessarily includes a circuit for changing the infrared power level incident on the phosphor.

WHAT WE CLAIM IS:—

1. An electroluminescent apparatus for producing radiation in the visible spectrum including an electroluminescent device comprising a semiconductor p-n junction diode capable of producing infrared radiation within the absorption spectrum for Yb^{3+} when biased, said diode being provided with a phosphor on a surface thereof for converting the infrared radiation to radiation in the visible spectrum said phosphor containing the cation pair Yb^{3+}—Er^{3+}, wherein the said phosphor has either at least two anion sites per unit cell which are differently populated in at least one percent of the unit cells of the said phosphor, or at least one anion vacancy per unit cell in at least one percent of the unit cells of the phosphor and wherein the phosphor consists of a fluorohalide, the halide in the fluorohalide being other than fluoride, or an oxyhalide or a mixture thereof, the phosphor containing either a cation percent of from 1/16 cation % Er^{3+} to 20 cation % Er^{3+} and from 5 cation % Yb^{3+} to 50 cation % Yb^{3+}, or from 1/16 cation % Er^{3+} to 20 cation % Er^{3+} and 1/50 cation % Ho^{3+} to 5 cation % Ho^{3+} together with at least 5 cation % Yb^{3+} and in which the said phosphor is capable of converting said infrared radiation to visible emission by at least a two excitation process each producing a different emission wavelength and each of which process involves a multiphoton process which is at least a two stage excitation, and in which the electroluminescent device is in combination with a circuit for varying the power level of said infrared radiation so as to alter the relative amounts of visible radiation produced by the said two processes.

2. An apparatus as claimed in claim 1, wherein the phosphor includes at least a 1/4 cation % Er^{3+}.

3. An apparatus as claimed in claim 1 or claim 2, wherein the phosphor includes not more than 2 cation % Er^{3+}.

4. An apparatus as claimed in any one of claims 1—3, wherein the phosphor includes not more than 2 cation % Ho^{3+}.

5. An apparatus as claimed in claim 1, wherein the phosphor contains at least 10 cation percent of Yb^{3+} based on the total cation content of the phosphor.

6. An apparatus as claimed in any one of the preceding claims wherein the said compound is an oxychloride compound.

7. An apparatus according to claim 6, wherein the said oxychloride compound has an oxygen to chlorine ratio of less than one.

8. An electroluminescent apparatus as claimed in claim 1, and substantially as hereinbefore described with reference to the accompanying drawing.

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1317731 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

FIG. 2

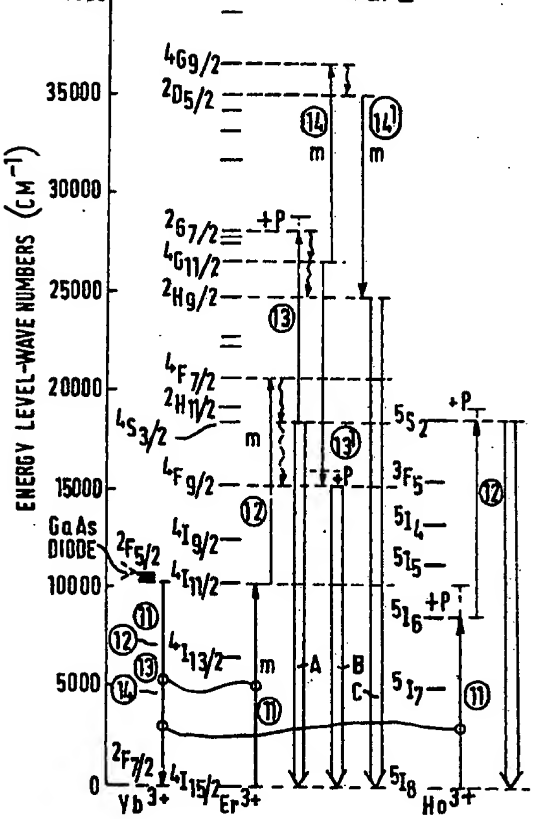

FIG. 1